

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
19 April 2001 (19.04.2001)

PCT

(10) International Publication Number
WO 01/27162 A2

(51) International Patent Classification⁷:

C08F

(21) International Application Number: PCT/US00/26245

(22) International Filing Date: 10 October 2000 (10.10.2000)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

09/414,497

8 October 1999 (08.10.1999) US

(71) Applicant (for all designated States except US): **ADHESIVES RESEARCH, INC. [US/US]**; P.O. Box 100, Glen Rock, PA 17327 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **ZAJACZKOWSKI, Michael, J. [US/US]**; 2595 West Philadelphia Street, York, PA 17404 (US).

(74) Agent: **HELLWEGE, James, W.; Birch Stewart, Kolasch & Birch, LLP, P.O. Box 747, Falls Church, VA 22040-0747 (US).**

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— Without international search report and to be republished upon receipt of that report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/27162 A2

(54) Title: NON-CORROSIVE, LOW VOLATILES CONTAINING STRIPPABLE GRAFT COPOLYMER PRESSURE SENSITIVE ADHESIVE

(57) Abstract: A crosslinked, non-corrosive, low volatiles-containing, strippable graft copolymer pressure sensitive adhesive is provided comprised of a backbone polymer having a polymeric moiety grafted thereto. The crosslinked copolymer comprises at least one A monomer consisting of a monomeric (meth)acrylic acid ester of a non-tertiary alcohol, optionally at least one B monomer, at least one polymereic graft moiety C having a T_g greater than 20 °C, and a macromeric graft moiety D containing repeat hydrophilic units.

NON-CORROSIVE, LOW VOLATILES CONTAINING
STRIPPABLE GRAFT COPOLYMER PRESSURE
SENSITIVE ADHESIVE

BACKGROUND OF THE PRESENT INVENTION

The present invention is directed to a crosslinked, non-corrosive, low volatiles-containing removable graft copolymer pressure sensitive adhesive.

Polymeric compositions are known which are comprised of backbone polymers having grafted thereto pendant polymeric moieties. The type of backbone polymer and graft polymeric moiety employed varies depending upon the desired characteristics of the end product. See, for example, U.S. Patent Nos. 3,786,116; 3,832,423; 3,842,146; 3,862,077; 3,879,494; 3,928,255; 3,989,768; 4,085,168; 4,551,388; 4,554,324; 4,656,213; 4,693,776; 4,732,808; 4,871,812; 5,352,516; 5,703,169; and 5,703,170. These patents disclose various types of such polymers which may or may not exhibit pressure sensitive adhesive properties.

Typical of the type of polymeric compositions disclosed in the above patents are compositions comprised of a backbone polymer such as an acrylic or methacrylic backbone polymer having attached thereto a graft polymer comprised of a polymerizable macromolecular monomer such as styrene or alpha-methylstyrene. See, for example, U.S. Patent No. 4,554,324, and commonly-assigned U.S. Patent Nos. 5,352,516; 5,703,169; 5,703,170; among others, in this regard.

The acrylic pressure sensitive adhesives such as described in U.S. Patent No. 4,554,324 and U.S. Patent No. 5,352,516 may be made from an acrylic ester and a polar acrylic monomer. The polar acrylic monomer can be one or a mixture of acrylic acid, acrylamide, acrylonitrile, itaconic acid, etc. The acrylic ester can be any aliphatic ester of acrylic acid. Such monomers are typically polymerized free radically by solution, suspension or emulsion polymerization. The acrylate portion of the copolymer is generally present in a generally high concentration and renders the polymer tacky. The polar monomer increases the ability of the adhesive to bond to a surface.

While such polymeric compositions have been found to have utility as pressure sensitive adhesives, one area that has not heretofore been addressed with much success is providing high performance pressure sensitive adhesives which may be suitable for use at high temperature environments (i.e., environments where the temperature exceeds about 250° F.). Recent advances in the electronics industry also require the use of non-corrosive pressure sensitive adhesives due to the sensitivity of the electronic components. It is also desirable for the adhesive to have a low-volatiles content to minimize contamination during use of such adhesives during the manufacture of computer assemblies as well as being easily removable. It has been found that conventional polar monomer-containing pressure sensitive adhesives do not provide satisfactory performance at high temperatures. It has also been found that such adhesives exhibit undesirable corrosive properties as well

as contain an undesirable volatiles content (thus leading to potential contamination during electronics manufacturing).

OBJECTS AND SUMMARY OF THE PRESENT INVENTION

It is accordingly an object of the present invention to provide a strippable pressure sensitive adhesive.

It is also another object of the present invention to provide a pressure sensitive adhesive which is non-corrosive and has a low volatiles content.

In accordance with the present invention, there is thus provided a crosslinked, non-corrosive, low volatiles-containing strippable graft copolymer pressure sensitive adhesive comprised of a backbone polymer having a polymeric moiety grafted thereto, said graft copolymer comprising the crosslinked reaction product of:

- (1) at least one A monomer consisting of a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, said alcohol having from 4 to 12 carbon atoms,
- (2) optionally at least one B monomer different from the A monomer,
- (3) at least one polymeric graft moiety C having a T_g greater than 20°C, and
- (4) at least one polymeric graft moiety D containing repeat hydrophilic units, preferably a polyether or polyester-based graft moiety.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is a crosslinked graft colymer pressure sensitive adhesive comprised of a backbone polymer having a polymeric moiety grafted thereto. The graft copolymer comprises the crosslinked reaction product of at least one A monomer (as defined), optionally at least one B monomer, at least one polymeric graft moiety C having a T_g greater than 20 °C, and at least one polymeric graft moiety D containing repeat hydrophilic units.

The graft copolymer includes at least one A monomer consisting of a monomeric (meth)acrylic acid ester of a non-tertiary alcohol where the alcohol portion has from 4 to 12 carbon atoms. Exemplary A monomers include but are not limited to esters of acrylic acid or methacrylic acid with non-tertiary alcohols such as 1-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol, 3,5,5-trimethyl-1-hexanol, 3-heptanol, 2-octanol, 1-decanol, 1-dodecanol, etc.

Optionally, one or more polymerizable B monomers may be incorporated in the copolymer which B monomer(s) is copolymerizable with the A monomer. Preferably, the B monomer is a non-polar monomer comprising a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol having from 1 to 3 carbon atoms, such as methyl(meth)acrylate, ethyl(meth)acrylate, n-propyl(meth)acrylate, and isopropyl(meth)acrylate. Additional B monomers include vinyl acetate and aromatic monomers such as styrene. It has been found that the presence of a polar B monomer

(such as acrylic acid) in pressure sensitive adhesives is a disadvantage to the extent that a non-corrosive adhesive is desired or that the volatiles content of the adhesive is to be minimized. The graft copolymer of the present invention thus contains no more than about 5 wt. % polar B monomers, based on the total weight of the reactants. Preferably, any polar B monomer which is present includes alcohol, amide, amine and/or acid functionalities to permit crosslinking to occur by means of such functionalities.

The graft polymeric moiety C has a T_g greater than 20°C. Graft polymeric moiety C has the formula X-Z wherein X is a group copolymerizable with monomers A and B or capable of attachment to copolymerized A and B monomers and Z is a polymeric graft moiety having a T_g greater than 20°C. The Z moiety is essentially unreactive under copolymerization conditions.

More specifically, the X moiety is an unsaturated polymerizable moiety the composition of which is not critical. The X moiety may be, for example, when intended to be copolymerizable with monomers A and B, simply a vinyl group of the formula CHR=CR^1- where R is hydrogen or COOH and R^1 is hydrogen or alkyl such as methyl. Other exemplary X moieties include but are not limited to methacryloyl, maleoyl, itaconoyl, crotonoyl, unsaturated urethane moiety, methacrylamido and moieties of the formula $\text{CH}_2=\text{CHCH}_2\text{O}-$.

The X moiety may comprise an amine or alcohol moiety (such as a monohydroxyl or monoamine moiety) which permits attachment of the macromer to a suitable functionality on previously-

polymerized monomers A and B. For instance, the hydroxyl moiety can serve as a terminal reactive group by reaction with suitable moieties on the polymer backbone resulting from the use of monomers such as isocyanate-substituted (meth)acrylic acid, (meth)acrylic acid anhydride, etc.

A variety of functional groups may be employed to attach the graft Z to the polymer backbone.

Exemplary functional groups include but are not

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{C-O-CHR-CH}_2\text{-} \end{array}$$

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{C-O-CH}_2\text{CH}_2\text{-NH-C-O-CHR-CH}_2\text{-} \end{array}$$

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{C-O-CHR-CH}_2\text{-} \end{array}$$

 limited to -C-O-CHR-CH₂- ; -C-O-CH₂CH₂-NH-C-O-CHR-CH₂-

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{C-O-CHR-CH}_2\text{-} \end{array}$$

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{O-C-CH}_2\text{-O-CHR-CH}_2\text{-} \end{array}$$

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{OCH}_2\text{CH}_2\text{-O-CHR-CH}_2\text{-} \end{array}$$

where R is a hydrogen atom or a lower alkyl group.

With regard to the polymeric graft moiety C portion of the adhesive composition, U.S. Patent Nos. 3,786,116; 3,842,057; 3,842,058; 3,842,059; 3,862,098; 3,862,101, 3,862,102 and 4,554,324 disclose polymerizable macromers which are suitable for use as graft moieties on a backbone polymer as defined.

Preferably, the polymeric moiety C is formed from a vinyl aromatic monomer such as styrene, alpha-methylstyrene, indene and p-tert-butylstyrene. However, the polymeric moiety Z may also be formed from vinyl toluene, acenaphthalene, acrylonitrile and methacrylonitrile; organic isocyanates including lower alkyl, phenyl,

lower alkyl phenyl and halophenyl isocyanates; organic diisocyanates including lower alkylene, phenylene, and tolylene diisocyanates; lower alkyl and allyl acrylates and methacrylates, including methyl, t-butyl acrylates, and methacrylates; lower olefins, such as ethylene, propylene, butylene, isobutylene, pentene, hexene, etc.; vinyl esters of aliphatic carboxylic acids such as vinyl acetate, vinyl propionate, vinyl octoate, vinyl oleate, vinyl stearate, vinyl benzoate, vinyl lower alkyl ethers; conjugated dienes such as isoprene and butadiene; 2-oxazolines such as 2-ethyl-2-oxazoline; and vinyl unsaturated amides such as acrylamide, methylacrylamide, N,N-di(lower alkyl) acrylamides such as N,N-dimethylacrylamide.

The selection of the specific polymerizable monomer for the polymer graft is not critical, since as the above listing suggests, a wide variety of monomers (and the resulting polymeric moieties) can be used with success as a polymeric graft in the claimed composition which meet the minimum T_g requirement.

The molecular weight of the graft polymeric moiety C is preferably sufficient to result in the formation of a "phase-separated" graft copolymer composition. Generally the molecular weight of the graft polymeric moiety will be within the range of from about 2,000 to 60,000, and will preferably range from about 2,000 to 13,000.

The graft polymeric moiety D also forms polymeric sidechains on the copolymer. The macromer D contains repeat hydrophilic units.

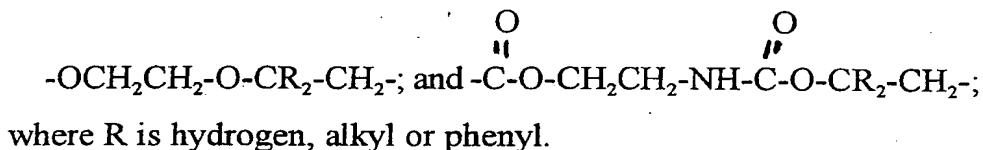
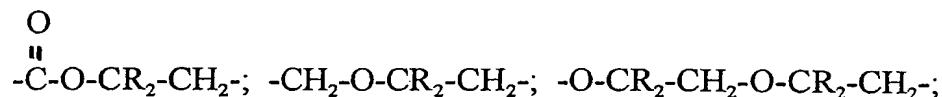
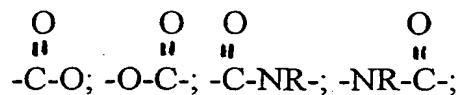
The macromer D may be represented by the formula X-(Y)_p-Z-R. X is as defined above and is a moiety copolymerizable with

monomers A and B or, in the alternative, capable of attachment to polymerized monomers A and B, Y is a divalent linking group, Z is a homo- or copolymeric moiety essentially unreactive at copolymerization conditions containing repeat hydrophilic units, R is a terminal group, and p is 0 or 1.



A preferred Y divalent linking group is $-\text{C}-$, or a linking group which incorporates such a moiety.

Additional Y linking groups which may be employed in connection with the present invention include but are not limited to the following moieties:



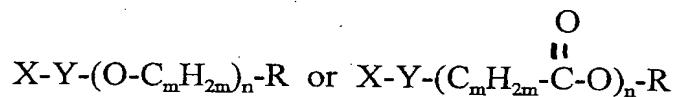
Obviously, the presence of the Y linking group is optional in the event the moiety includes a functionality which enables the Z moiety to react with the X moiety. As the incorporation of macromolecular moieties in copolymers is well understood by those skilled in the art, the choice of a suitable X and Y moiety for use in

the present invention may be readily made upon practice of the present invention. See, for example, the discussion in U.S. Patent Nos. 3,786,116; 3,832,423; 3,842,058; 3,842,059; 3,842,146; and 4,554,324, herein incorporated by reference.

The Z moiety is preferably selected from the group consisting of (but not limited to) a polyalkylene oxide radical, a polyethyloxazoline radical such as a radical of poly(2-ethyl-2-oxazoline), polyvinylpyrrolidone radical, polyester(meth)acrylate radical, polyvinyl caprolactam radical, polymethylvinyl ether radical or mixtures thereof. Exemplary D macromers formed from such radicals include but are not limited to ethoxylated or propoxylated hydroxy(C₁₋₅)alkyl meth(acrylate), polymethylvinyl ether mono(meth)acrylate and beta-carboxyethyl acrylate. The molecular weight of the macromer used in the present invention is not critical but will generally range from about 300 to about 50,000, and preferably from about 300 to 3,000.

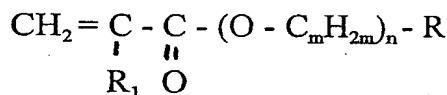
The Z moiety is preferably comprised solely of one or more hydrophilic monomer radicals. However, the Z moiety may also be a copolymer of hydrophilic and hydrophobic monomers. Desirably, any non-hydrophilic portion employed in the D macromer is present in an amount of 50% or less based on the weight of the macromer.

The macromer D is preferably represented by the formula:



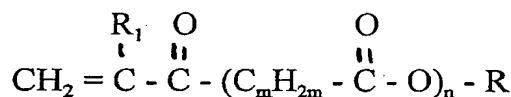
wherein X and Y are as defined above and R represents a terminal group; and in which m is an integer of from 2 to 6, and n ranges up to 300.

More specifically, macromer D may be an ethoxylated or propoxylated hydroxy(C₁₋₅)alkyl (meth)acrylate represented by the formula:



wherein R₁ is hydrogen or C₁₋₅ alkyl and R is a terminal group. Preferably, m is 2 or 3 and n is 4 to 30, and R is H, OH, C₁₋₅ alkyl, or nonyl-phenol.

Alternatively, macromer D may advantageously comprise a 2-carboxy(C₁₋₅)alkyl acrylate of the formula:



where R₁ is hydrogen or C₁₋₅ alkyl and R is a terminal group. Preferably, m is 2 or 3 and n is 4 to 30, and R is H, OH, C₁₋₅ alkyl or nonyl-phenol.

Of course, macromer D may incorporate mixtures of polyether and polyester repeat units with advantage in a variety of ratios. Such ratios are non-critical to practice of the present invention.

The macromer D may employ a variety of terminal groups R. While the terminal group may typically be OH or C₁₋₅ alkyl, it may be desirable to select a terminal group based on the functional character of the terminal group. For instance, suitable terminal

groups include but are not limited to (1) acid/ionic groups such as carboxyl, phosphate or sulfate groups, (2) hydrophobic groups such as lower alkyl, phenyl or substituted phenyl, and (3) hydrophilic groups such as hydroxyl or amine groups.

Depending upon the terminal group employed, ionic end groups may be used to provide pH-dependent solubility characteristics for the copolymer. Hydrophobic terminal groups may be used to reduce the water sensitivity of the copolymer.

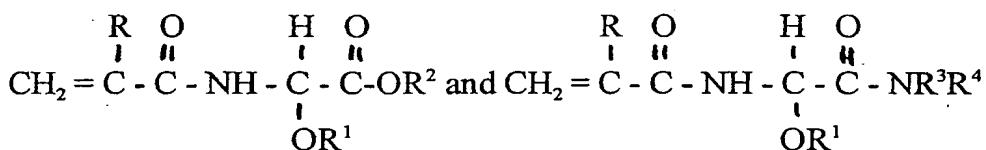
Other physical properties or characteristics of the copolymer may be modified by selection of suitable terminal groups. The copolymer of the present invention may be covalently or ionically-crosslinked in a conventional manner. Ionic terminal groups may be used to provide a desired degree of crosslinking; for example, by neutralizing acid moieties with metal hydroxides. High temperature performance may be enhanced by incorporating an acid functionality in conjunction with a ditertiary amine. Aqueous solution viscosities may be influenced by the presence of ionic terminal groups.

The graft copolymer of the present invention may be crosslinked by use of a suitable internal or external crosslinking agent, the identity of which is not particularly critical to practice of the claimed invention.

Exemplary internal crosslinking agents are disclosed in U.S. Patent Nos. 3,714,096; 3,923,931; 4,454,301; 4,950,708; 5,194,486; 5,214,094; 5,420,195; and 5,563,205, each herein incorporated by reference. Exemplary internal crosslinking agents include polyfunctional compounds having at least two non-conjugated

carbon-to-carbon double bonds. Exemplary polyfunctional compounds include but are not limited to diallyl maleate, diallyl phthalate, and multifunctional acrylates and methacrylates (such as polyethylene glycol diacrylate, hexane diol diacrylate, ethoxylated trimethylolpropane triacrylate, pentaerythritol triacrylate, propylene glycol diacrylate and trimethylolpropane trimethylacrylate. Such crosslinking agents are disclosed in U.S. Patent Nos. 5,420,195 and 5,563,205, each herein incorporated by reference.

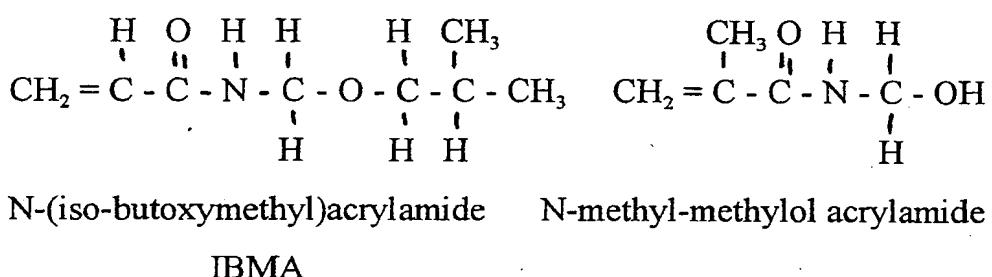
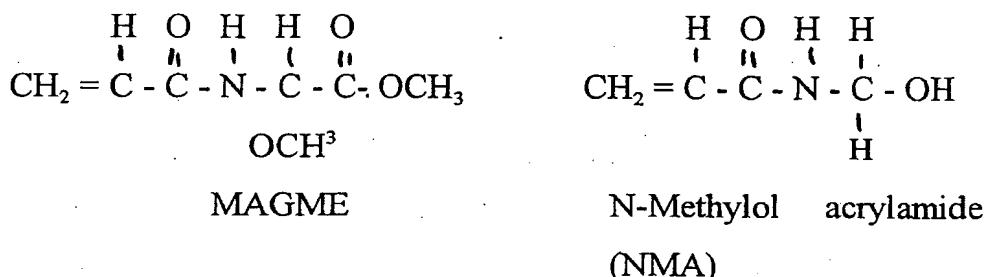
Other suitable internal crosslinking agents include (1) alkyl acylamidoglycolate alkyl ethers or acylamidoglycoamide alkyl ethers having the formulae



where R is hydrogen or methyl, R¹ is C₁₋₆ alkyl, C₅₋₆ cycloalkyl, R² is C₁₋₆ alkyl and C₅₋₆ cycloalkyl, each of which may be optionally substituted by oxygen or nitrogen heteroatoms, and R³ and R⁴ are hydrogen or C₁₋₂₀ alkyl or cycloaliphatic alkyls optionally substituted with nitrogen or oxygen moieties, (2) acetoacetoxyalkyl (meth)acrylates and isoalkoxy (meth)acrylamides, and (3) alkoxides of a central atom further substituted with a polymerizable methacrylyl function, wherein the central atom is selected from the group consisting of Groups II, III or IV, such as methacryloxyalkyl silanes having at least one alkoxy group. Such crosslinking agents are

disclosed in U.S. Patent Nos. 4,454,301; 5,194,486; and 5,214,094, each herein incorporated by reference. Alternatively, the crosslinking agent may be acetoacetoxyalkyl (meth)acrylate and N-methylolacrylamide.

By way of specific example, the following internal crosslinking agents may be employed:



Combinations of two or more of the above internal crosslinking agents may be employed with advantage.

External crosslinking agents may also be employed with advantage to crosslink the graft copolymer through functionalities on either the polar B monomer or on the graft polymeric moieties. Such crosslinking agents include without limitation melamine resins, melamine-formaldehyde resins, aziridine compounds and diamines.

Preferably, the A monomer is present in the graft copolymer in an amount of from 30 to 95 percent by weight, the optional non-polar B monomer is present in an amount of from 0 to 50 percent by weight, the C macromer is present in an amount of from 12 to 15 percent by weight, the D macromer is present in an amount of from 3 to 50 percent by weight, and the internal crosslinking agent (if employed) is present in an amount of from 0.1 to 7 percent by weight, based on the total weight of the respective components in the graft copolymer.

As noted above, the copolymer composition of the present invention may be prepared by any conventional polymerization technique, including (1) free radical-initiated copolymerization of components A, C and D and optionally B in the presence of a solvent and the crosslinking agent(s), or (2) attachment of the macromer grafts to a preformed crosslinked backbone polymer formed from copolymerized monomer A optionally copolymerized with monomer B via reaction with a suitable functional group on the backbone polymer subsequent to formation of same. Suitable copolymerization temperatures range from about 20°C. to about 150°C. for periods of time of from 2 to 24 hours until the desired degree of conversion occurs. Upon completion of the copolymerization process, the solvent is removed and a tacky copolymer results having acceptable adhesive properties.

The adhesive of the present invention may be used in association with a variety of body members (e.g., tapes, patches, strips, labels, etc.) to provide an adhesive assembly. For example, the

body member may be in the form of a backing material coated on at least one side thereof with the adhesive to provide an adhesive-backed sheet film or tape. Exemplary backing materials used in the production of such a product include but are not limited to flexible and inflexible backing materials conventionally employed in the area of pressure sensitive adhesives, such as creped paper, kraft paper, fabrics (knits, non-wovens, wovens), foil and synthetic polymer films such as polyethylene, polypropylene, polyvinyl chloride, poly(ethylene terephthalate) and cellulose acetate, as well as glass, ceramics, metallized polymer films and other compatible sheet or tape materials.

The body member (e.g., in sheet form) may be coated in any conventional manner with the adhesive composition of the present invention, such as by roll coating, spray coating, extrusion coating, co-extrusion coating, hot melt coating by use of conventional coating devices. When appropriate, the adhesive of the present invention may be applied as a solution to at least one surface of the body member and the solvent subsequently removed to leave a tacky adhesive residue on the body member. The adhesive may be applied to the body member either in the form of a continuous layer or in discontinuous form.

The present invention is exemplified in the following examples which are intended to be explanatory in nature and not limiting in scope of the present invention.

EXAMPLE 1

A one liter baffled reactor is heated to 115 to 120 °F, and purged with nitrogen. The following reaction mixture is provided:

Isooctyl acrylate (A monomer)	260.48 grams
Ethoxylated nonyl phenol acrylate (macromer D)	52.80 grams
Polystyrene macromer (macromer C)	26.40 grams
N-methylolacrylamide (internal crosslinker)	3.52 grams
2-(acetoacetoxy) ethyl methacrylate (internal crosslinker)	8.80 grams
VAZO 52 catalyst	1.08 grams
Solvent (22% butyl acetate, 65%) heptane, 13% isopropyl alcohol)	448 grams

30 % of the above reaction mixture is initially added to the reactor. The remaining portion of the reactor charge is added incrementally over 4 hours. At the completion of the reactant addition, the reaction is permitted to continue for another 1.5 hours to form a crosslinked strippable pressure sensitive adhesive.

EXAMPLE 2

A one liter baffled reactor is heated to 120 to 125 °F, and purged with nitrogen. The following reaction inventive is provided:

Isooctyl acrylate (A monomer)	153.0 grams
Ethoxylated nonyl phenol acrylate (macromer D)	34.0 grams
Polystyrene macromer (macromer C)	25.50 grams

Methyl acrylate (B monomer)	115.60 grams
N-methylolacrylamide (internal crosslinker)	3.40 grams
2-(acetoacetoxy) ethyl methacrylate (internal crosslinker)	8.50 grams
VAZO 52 catalyst	1.45 grams
Solvent (22% butyl acetate, 65%)	
heptane, 13% isopropyl alcohol	460 grams

30 % of the above reaction mixture is initially added to the reactor. The remaining portion of the reactor charge is added incrementally over 4 hours. At the completion of the reactant addition, the reaction is permitted to continue for another 1.5 hours. The reactor temperature is increased to 130 to 135°F over the last two hours. At the conclusion of the reaction a pressure sensitive adhesive is formed.

WHAT IS CLAIMED IS:

1. A crosslinked, non-corrosive, low volatives-containing, strippable graft copolymer pressure sensitive adhesive comprised of a backbone polymer having a polymeric moiety grafted thereto, comprising the crosslinked reaction product of:
 - (1) at least one A monomer consisting of a monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol, said alcohol having from 4 to 12 carbon atoms,
 - (2) optionally, at least one B monomer different from monomer A, with the proviso that any polar B monomer which is present is present in an amount no greater than about 5 wt. %, based on the total weight of the reactants;
 - (3) at least one polymeric graft moiety C having a T_g greater than 20°C, and
 - (4) at least one graft macromer D containing repeat hydrophilic units.
2. The copolymer of claim 1 wherein said graft moiety C is a polymerized monoalkenyl-substituted aromatic hydrocarbon.
3. The copolymer of claim 2 wherein said polymerized monoalkenyl-substituted aromatic hydrocarbon comprises polystyrene.
4. The copolymer of claim 1 wherein the molecular weight of said graft moiety C is in the range of from about 2,000 to 30,000.

5. The copolymer of claim 1 wherein said at least one A monomer comprises an ester of acrylic or methacrylic acid with a non-tertiary alcohol selected from the group consisting of 1-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol, 3,5,5-trimethyl-1-hexanol, 3-heptanol, 2-octanol, 1-decanol, and 1-dodecanol.

6. The copolymer of claim 1 wherein the A monomer is present in the copolymer in an amount within the range of from about 30 to 95 percent by weight.

7. The copolymer of claim 1 wherein a B monomer is present which comprises an internal crosslinking agent.

8. The copolymer of claim 1 wherein the D macromer is present in the copolymer in an amount within the range of from about 3 to 50 percent by weight.

9. The copolymer of claim 1 wherein said macromer D is defined by the formula $X-(Y)_p-Z-R$, wherein X is a moiety copolymerizable with monomers A and B or capable of attachment to copolymerized monomers A and B, Y is a divalent linking group, Z is a homo- or

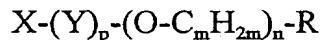
copolymeric moiety containing repeat hydrophilic units, R is a terminal group, and p is 0 or 1.

10. The copolymer of claim 9 wherein X is a (meth)acrylate moiety.

11. The copolymer of claim 1 wherein macromer D is a polyether or polyester (meth)acrylate moiety.

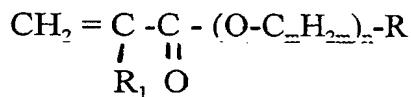
12. The copolymer of claim 9 wherein Z is selected from the group consisting of a polyalkylene oxide radical, a polyethyloxazoline radical, a polyacrylic acid radical, a polyvinyl alcohol radical, a polyvinylpyrrolidone radical, a polyvinylcaprolactam radical and a polymethylvinyl ether radical.

13. The copolymer of claim 1 wherein said macromer D is defined by the formula:



wherein X is a moiety copolymerizable with monomers A and B or capable of attachment to copolymerized monomers A and B, Y is a divalent linking group, R is a terminal group, m is an integer of from 2 to 6, n is an integer of up to 300, and p is 0 or 1.

14. The copolymer of claim 13 wherein said macromer D is defined by the formula



wherein R₁ is hydrogen or C₁₋₅ alkyl and R is a terminal group.

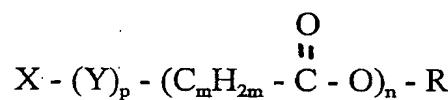
15. The copolymer of claim 14 wherein R is OH or C₁₋₅ alkyl.

16. The copolymer of claim 1 wherein said macromer D is selected from the group consisting of ethoxylated hydroxy (C₁₋₅ alkyl) acrylate, propoxylated hydroxy (C₁₋₅ alkyl) acrylate, ethoxylated hydroxy (C₁₋₅ alkyl) methacrylate, and propoxylated (C₁₋₅ alkyl) methacrylate.

17. The copolymer of claim 1 wherein said macromer D is selected from the group consisting of ethoxylated and propoxylated hydroxy (C₁₋₅ alkyl) (meth)acrylate, poly(2-ethyl-2-oxazoline), polyacrylic acid, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl caprolactam and polymethylvinyl ether mono(meth)acrylate.

18. The copolymer of claim 1 wherein said macromer D is 2-carboxy(C₁₋₅)alkyl acrylate.

19. The copolymer of claim 1 wherein said macromer D is defined by the formula:



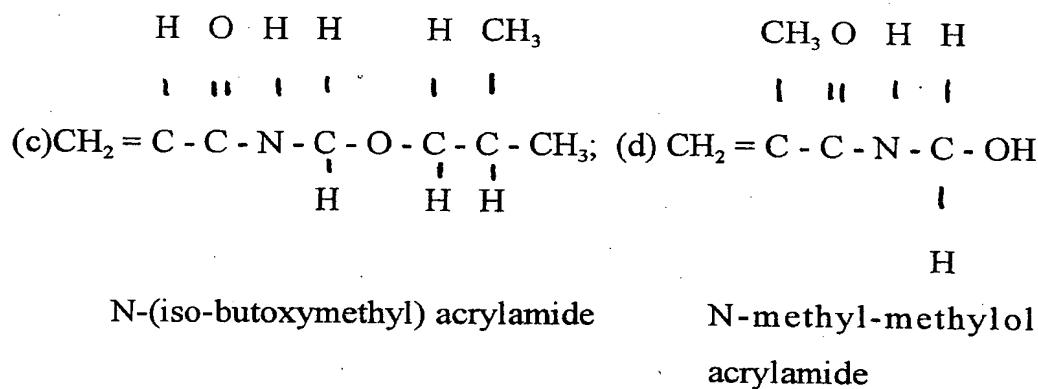
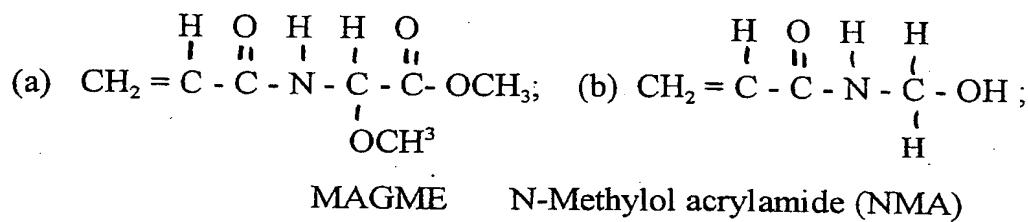
wherein X is a moiety copolymerizable with monomers A and B or capable of attachment to copolymerized monomers A and B, Y is a divalent linking group, R is a terminal group, m is an integer of from 2 to 6, n is an integer of up to 300, and p is 0 or 1.

20. The copolymer of claim 19 wherein R is OH or C_{1-5} alkyl.

21. The copolymer of claim 1 wherein a B monomer is present comprising at least one monomeric acrylic or methacrylic acid ester of a non-tertiary alcohol having from 1 to 3 carbon atoms.

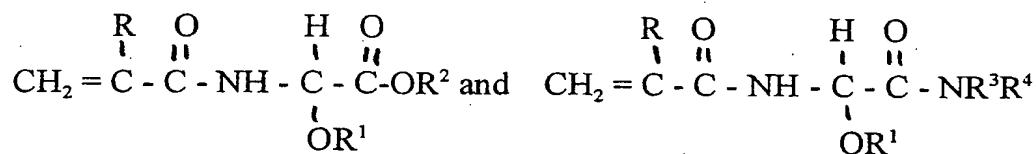
22. The copolymer of claim 21 wherein said B monomer is present in an amount of from 0 to 50 percent by weight.

23. The copolymer of claim 7 wherein said internal crosslinking agent is selected from the group consisting of:



24. The copolymer of claim 23 wherein said internal crosslinking agent is used in conjunction with acetoacetoxyalkyl(meth)acrylate.

25. The copolymer of claim 7 wherein said internal crosslinking agent is selected from the group consisting of (1) alkyl acylamidoglycolate alkyl ethers and acylamidoglycoamide alkyl ethers having the formulae:



respectively, where R is hydrogen or methyl, R¹ is C₁₋₆ alkyl, C₅₋₆ cycloalkyl, R² is C₁₋₆ alkyl and C₅₋₆ cycloalkyl, each of which may be optionally substituted by oxygen or nitrogen heteroatoms, and R³ and R⁴ are hydrogen or C₁₋₂₀ alkyl or cycloaliphatic alkyls optionally substituted with nitrogen or oxygen moieties, (2) acetoacetoxyalkyl (meth)acrylates, (3) isoalkoxy (meth)acrylamides, and (4) alkoxides of a central atom further substituted with a polymerizable methacrylyl function, wherein the central atom is selected from the group consisting of Groups II, III or IV.

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